Synthesis of Ag –TiO₂ Thin Films by Spin Coating process

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ABSTRACT:
In this research, Sol-gel technique prepared Ag–TiO₂ nano-composite thin films, which were deposited onto a glass substrate by the spin coating process. The microstructures and chemical ingredients of the obtained thin films were characterized by UV-visible spectroscopy (UV), Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FT-IR). It was discovered that the silver nano-particles completely joined to the TiO₂ matrix, where those nanoparticles distributed uniformly. In this way, the molar percent of the silver nitrate watery solution dominated the morphology of the thin film. Ag-TiO₂ Nano composite is very useful for expanding antibacterial of nanomaterials purpose.

Keywords: Nano TiO₂-Silver; Spin Coater; Thin Films.

INTRODUCTION
Researchers have demonstrated fixed interest in evolving antimicrobial substances including various organic chemical antibiotics and inorganic materials. The functional materials have a highly distinctive characteristics and ability of biological purpose, fore that the nanosized particles of organic and inorganic materials have attracted in order to raise attention in medical applications, especially when they became among those fine materials [1, 2]. Because of non-toxicity, it's high and fixed oxidizing power, long-range of the physical and chemical steadiness, of the most efficacious photocatalysis of which used these days is Titanium dioxide (TiO₂). The main features of inorganic antibacterial agents improved safely and firmness, comparing with organic antimicrobial materials [3, 4]. TiO₂ shows strong bactericidal activity, especially when exposed to irradiation close to UV light [5]. It has to be a reaction among the photo generated pits and electrons by way of aqua and oxygen consecutively, such as hydroxyl radicals (-OH) singlet oxygen (O₂.), and hydrogen peroxide (H₂O₂). Bacteria and the degradation of the toxic compounds which resulted from the bacteria itself could be finished off by TiO₂ and its deposits [6, 7].

It is worth to mention that, absolute oxidation can be accomplished for an entire cells and organic compounds of carbon dioxide [8], but still its defects like, its actual uses are obstructed by low quantity yields and the deficiency of visibility-light usage [9, 10]. For the purpose of finding solutions to overcome these obstacles, the use of silver by adding it to nanoparticles, exceedingly promoted the photocatalytic efficiency of TiO₂, where at Schottky barrier at each one of Ag–TiO₂ of get in contact with the region, it is noticed that its ability enabled it to confine electrons, and that decreases the assembly of light at the TiO₂ face. [11, 12]. Thus more electrons would be transferred due to the enhancement of charge separation. A silver metal and its solutions considered as anantibacterial materials and have a low toxicity against cells, that feature made it as an effective antimicrobial factor for centuries [13]. Generally, silver ions react in the company of proteins leading to the inactivation of the proteins via responding by way of the SH bands of which existent in bacteria is the first of two effects of silver on bacterial cells, and the second, that silver ions can interact in the midst of DNA of bacteria, stopping a cell proliferation. Both the effects produce to kill the bacterial cells. All of
what mentioned in respect with, were reported by several studies to explain that damping impact 
of silver on bacteria [14, 15].

On the other hand, regarding to the usage of silver ions, it is well known that Silver-doped 
another materials are chemically sturdy and liberate silver ions for a long period. Especially 
when silver crystal size is decreased, where the effect of silver nanoparticles became long term, 
steady and its release could be controlled. To carry out as a magnificent antibacterial coating 
inside the water disinfection, nourishment manufacturing as well as others in related those fields 
[16, 17]. The researchers sought to find manufacturing systems by combining the titanium and 
silver nanoparticles in order to use the TiO$_2$ on a larger scale in medical application, due to its 
significance in this field by expanding the nanometers antibacterial functions [18]. Synthesis of 
Ag/TiO$_2$ nanocomposites is accomplished by various synthetic methods. A solvothermal 
process in the literature review is usually utilized to acquire the nanoparticles. However for 
actual applications, exotic metal ions into TiO$_2$ particles and films is being presented by the sol–
gel process, which considered as the most effective method, for instance, the films that 
containing Ag$^+$ under UV exposure the photoreduction occurs [19], also immediate calcination 
of the sol gel substance [20]. But, photo reduced silver not possible to be entirely scattered 
inside the deepness under the TiO$_2$ face, principally once the adhesion force is feeble for the 
outside top of coating [18, 21]. Positively, the use of the sonochemical method suppressed 
those defects. Mixtures of solution were exposed to intensive ultrasonic irradiation in sol gel 
processes, and that was reported since the early 1980s [22].

In this research, the sol gel technique is the appropriate way to make Ag/TiO$_2$ thin films were 
deposited onto glass substrate with several of the silver content. It could be controlled the 
morphological composite films by setting the molar ratio of AgNO$_3$ watery solution to TiO$_2$, 
when introduced the silver ion Ag$^+$. Forming multiphase nanocomposite thin films in the 
Ag/Anatase supported the interaction between the nanosized silver particles and the TiO$_2$ grains.

Experimental Part:-

Materials:–

The materials used in this work Titanium (IV) isopropoxide (Aldrich Chemicals Ltd., USA), 
Ethanol alcohol and Silver nitrate (AgNO$_3$). All materials were used without further 
purification; In addition to used deionized water in all the preparations.

Preparation of Ag–TiO$_2$ Thin Film:

TiO$_2$ nanoparticles were doped with several % Ag prepared by sol-gel method. At first, 5gm 
of Titanium (IV) isopropoxide was dispersed in 100 ml of deionized water and ethanol alcohol 
at 25 °C. To this solution, Silver nitrate was diluted in water and added drop wise (the molar 
ratio of Ag to TiO$_2$ was ranged from 5: 1 to 25:1) and mixed by the magnetic stirrer for 1 h and 
the stirring was continued for 3 h at 70 °C. The solution was kept in dark for 24 h for gelation 
process. Droplets of the prepared solution was deposited onto washed glass substrate (20 × 10 
mm$^2$) by spin-coating at 2000 rpm for 40 s. The obtained films were dried at 80 °C for 2 h and 
then annealed at 450 °C for 1 h.

Physio-chemical characterization of Ag–TiO$_2$ Thin Film:

Surface plasmon resonances of the sample were analyzed with a UV-Vis Spectrophotometer 
(Cary 300 Conc spectrophotometer), the wavelength range from (200– 800nm) at room 
temperature. The morphology of the obtained thin films was characterized by using SEM 
microscope with EDAX type (VEGA3 TESCAN). The crystal structures of the thin films was 
examined by an X-ray diffraction (XRD) with Cu K$\alpha$ radiation ($\lambda$ = 1.54060 Å) operated at 30 
kV and 20 mA. The information to the particle size was obtained from the Sherrer Formula 
[23]:
D = 0.89 λ / β cos θ  
Where D is the average particle size, λ is the wavelength of X-ray, β is the full width at maximum half of diffraction peak and θ is angle of the diffraction.

The mean particle size of the Ag–TiO₂ nanoparticles was determined to be about 15 nm.

FTIR spectra of the Ag-TiO₂ nanocomposite was obtained (400 – 4000 cm⁻¹) from (IR Affinity-1 FTIR spectrometer). The essential IR groups, like (C-N), (O-H), (C-H), (C=C), (N-H), (C-O) and (C-H) their symmetric and lopsided stretching, and their extending frequencies were studied order to decide the existence of practical group in the ethyl acetate. (Ogunmwonyi et al., 2010).

Results and Discussion:-

The Ag–TiO₂ thin film appeared to be vivid ruby little clear which clearly indicates the formation of Ag–TiO₂ nanoparticles. The UV-Vis Spectra of the Ag–TiO₂ nanoparticles are given in Figure 1. from which it is clear that the Ag–TiO₂ surface plasmon occurred at 350 nm [23].

Figure 2.a and b, shows the SEM image of Ag–TiO₂ thin films samples at different the ratio of Ag to TiO₂ after drying and annealing at 450 °C for 1h. The images show all the particles at the nanometer scale. Figure 2.A. show there are a bright particles surrounding the dark which indicated that individual silver particle dispersed with the TiO₂ as product of Ag–TiO₂ nanocomposite is more agglomerate, growth and regularly distributed than the Morphology which is appeared in Figure 2.B. The EDX spectra indicated to presence a small amount of silver within the TiO₂, that confirms individual silver ions interacted with the TiO₂ matrix as shown in Figure 3.

The evidence for the formation of elemental Ag–TiO₂ thin film is provided by X-Ray diffraction (XRD) analysis in Figure 4. The spectrum shows five major diffraction intensity peaks these showed that the entire of the eventual films display a pure anatase phase structure. The peaks of silver at 2θ = 38.07° appeared at the same peak of the rutile TiO₂ and detected on 2θ = 44.25° and 64.38° to the crystalline of metal silver [20, 24]. The eventual x-ray diffraction results of the films exhibit that four peaks (1 0 1), (1 1 1), (1 0 5) and (2 2 1) for TiO₂ crystal planes, respectively. The peaks were observed to originate from planes of the sample respectively (JCPDS no: 73-0370).

The FTIR Spectral analysis of metal ions as shown in Figure 5. The sample shows certain common absorption bands the hydroxyl (O-H) and the presence (N-H) vibration frequency which are exchangeable at 3450 cm⁻¹ [24, 25]. Mutual vibration peaks at 2325 cm⁻¹ are characteristic of a (C-H) symmetrical band and stretching of hydrocarbon (C=O) at 1785 cm⁻¹. The absorption peak at 1635 cm⁻¹ is attributed to the O-H bending vibration. Band below 1250 cm⁻¹ is due to Ti-O-Ti and Ti-O-Ag vibrations which are appearing unsymmetrical [22, 25].

CONCLUSION:
The polycrystalline thin films of the Ag–TiO₂ were successfully synthesized on the glass substrate by the spin coating process. The morphology of the produced thin film might be controlled via different proportion of AgNO₃ in the direction of TiO₂ in the solution of which prepared previously. The liberation time of Ag⁺, increase the silver concentration in the samples lead to excellent raise in the cytotoxicity of the composite thin films will be extended by different Ag loadings with TiO₂. The regular distribution of the silver nanoparticles was discovered and entirely joint to the TiO₂ matrix. The synthesis process steps are not complex, suitable and inexpensive.
Figure 1 UV–Vis spectrum of Ag–TiO₂ thin film for molar ratio 25:1.

Figure 2 SEM images of Ag–TiO₂ thin film at different molar ratio: A. 25:1 Ag/TiO₂, B. 5:1 Ag/TiO₂ thin films.
Figure 3: Elemental analysis of Ag–TiO₂ thin film molar ratio 25:1.

Figure 4: The XRD analysis of Ag–TiO₂ thin film for molar ratio 25:1. A: anatase phase, R: rutile phase and Ag: metal silver.
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Figure 5: FTIR spectrum of Ag–TiO₂ nanocomposite for molar ratio 25:1

REFERENCES
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